



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/747,956	12/31/2003	Ulrich Seseke-Koyro	037110.51540D1	6209

23911 7590 06/01/2006

CROWELL & MORING LLP
INTELLECTUAL PROPERTY GROUP
P.O. BOX 14300
WASHINGTON, DC 20044-4300

EXAMINER

NGUYEN, NGOC YEN M

ART UNIT PAPER NUMBER

1754

DATE MAILED: 06/01/2006

Please find below and/or attached an Office communication concerning this application or proceeding.



UNITED STATES PATENT AND TRADEMARK OFFICE

Commissioner for Patents
United States Patent and Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450
www.uspto.gov

MAILED
JUN 01 2006
GROUP 1700

**BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES**

Application Number: 10/747,956
Filing Date: December 31, 2003
Appellant(s): SESEKE-KOYRO ET AL.

J. D. Evans
For Appellant

EXAMINER'S ANSWER

This is in response to the appeal brief filed March 21, 2006 appealing from the Office action mailed April 7, 2005.

(1) Real Party in Interest

A statement identifying by name the real party in interest is contained in the brief.

The examiner is not aware of any related appeals, interferences, or judicial proceedings which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

(3) Status of Claims

The statement of the status of claims contained in the brief is correct.

(4) Status of Amendments After Final

The appellant's statement of the status of amendments after final rejection contained in the brief is correct.

(5) Summary of Claimed Subject Matter

The summary of claimed subject matter contained in the brief is correct.

(6) Grounds of Rejection to be Reviewed on Appeal

The appellant's statement of the grounds of rejection to be reviewed on appeal is correct.

(7) Claims Appendix

The copy of the appealed claims contained in the Appendix to the brief is correct.

(8) Evidence Relied Upon

4,989,775	Shimajiri et al	02-1991
5,723,187	Popoola et al	03-1998
6,105,850	Lauzon et al	08-2000
WO 99/48641	Seseke-Koyro et al	09-1999

(9) Grounds of Rejection

The following ground(s) of rejection are applicable to the appealed claims:

Claims 8-11 are rejected under 35 U.S.C. 103(a) as being unpatentable over WO 99/48641 (to Seseke-Koyro et al) or Lauzon et al (6,105,850), either one in view of Popoola et al (5,723,187).

Seseke-Koyro discloses an alkali fluorozincate as a fluxing agent for aluminum or aluminum alloys (note claim 1). The alkali metal can be potassium (note claim 2).

Alternatively, Lauzon '850 is applied as stated below.

Lauzon '850 discloses that potassium fluorozincate can be used as a fluxing agent for aluminum brazing (note claim 1 and column 2, lines 34-41).

The process limitations in claims 8, 11 and 12 are noted. However, the instant claims are product-by-process claims, which are treated as product claims. Since the examiner has found a substantially similar product as in the applied prior art, the instant claims are rendered obvious. *In re Brown*, 173 USPQ 685 and *In re Fessmann*, 180 USPQ 324.

The difference is Seseke-Koyro or Lauzon '850 does not disclose that the particle size of the potassium fluorozincate.

Popoola '187 discloses in a process of using a flux to for bonding metals to aluminum substrate (note column 1, lines 7-10). The flux can be fluoride salts and the flux is desired to be applied as a solution and the particle size of the flux is controlled to less than 10 micrometers, with at least 70% of the salts being in the particle size range of 2-4 micrometers so that the particles remaining in suspension at all times without stirring (note column 2, lines 18-26). Particularly, Popoola '187 discloses that the fluoride salt is added to the sprayable medium in closely controlled particle size to minimize the need for stirring and to retain at least 25% by volume of the salt in suspension at all times. To this end, the salt particle is equal to or less than 10 microns with about 70% being 2-4 microns (note column 3, lines 42-50).

It would have been obvious to one of ordinary skill in the art to obtain potassium fluorozincate of either Seseke-Koyro or Lauzon '850, by optimizing the conditions of the process of making such product, or by pulverizing (if the product particles are too big) or agglomerating (if the product particles are too small), with the particle size of less than 10 micrometers as suggested by Popoola '187 because such particle size is desired in the art of using a flux in a brazing process.

Claim 12 is rejected under 35 U.S.C. 103(a) as being unpatentable over WO '461 or Lauzon '850 in view of Shimajiri et al (4,989,775).

Seseke-Koyro or Lauzon '850 is applied as stated above.

The difference is Seseke-Koyro or Lauzon '850 does not disclose the particle size for the potassium fluorozincate.

Shimajiri '775 discloses for a process of brazing aluminum components, a fluoride flux powder having a grain size of 15 microns on average is desirable (note column 4, lines 55-57).

It would have been obvious to one of ordinary skill in the art to obtain potassium fluorozincate of either Seseke-Koyro or Lauzon '850, by optimizing the conditions of the process of making such product, or by pulverizing (if the product particles are too big) or agglomerating (if the product particles are too small), with the particle size of 15 micrometers on average, as suggested by Shimajiri '775 because such particle size is desired in the art of using a flux in a brazing process.

(10) Response to Argument

1. Appellants argue that claims 8-12 are patentable because the primary and secondary references relate to distinctly different materials and there is no suggestion or motivation to combine these references.

Hereinafter, primary references refer to Seseke-Koyro and Lauzon; secondary references refer to Popoola and Shimajiri; flux, flux agent, and fluxing agent are used interchangeably.

Appellants argue that it would not have been obvious to combine the secondary references of Popoola or Shimajiri with either Seseke-Koyro or Lauzon because

Seseke-Koyro and Lauzon each relate to potassium fluorozincate salts while Popoola and Shimajiri disclose different aluminum-containing salts.

As stated in the above rejections, all references are related to the use of a fluxing agent (or a flux) to bond or braze aluminum substrates, note the English abstract of Seseke-Koyro; claim 1 of Lauzon '850; column 1, lines 7-10 of Popoola '187; claim 1 of Shimajiri '775. In Seseke-Koyro and Lauzon '850, potassium fluorozincate is clearly disclosed as a commercially available fluxing agent, which is suitable for brazing aluminum substrates. The difference is Seseke-Koyro and Lauzon '850 do not teach the particle size of such potassium fluorozincate. However, as suggested by Popoola '187 or Shimajiri '775, different methods can be used to apply the fluxing agent in the process of brazing aluminum substrates. When a wet method is used, i.e., using a slurry or suspension of the fluxing agent, small particle size is desirable as suggested by Popoola '187 and when a dry method is used, larger particle size is preferred as suggested by Shimajiri '775. Thus, it would have been obvious to one of ordinary skill in the art to apply the potassium fluorozincate fluxing agent, as disclosed in Seseke-Koyro or Lauzon '850 by either the wet process as suggested by Popoola '187 or by the dry process as suggested by Shimajiri '775 because these are known and conventional methods in the art and to select a proper particle size for the fluxing agent depending on process used.

It should also be noted that in Lauzon '850, the flux is preferred to be sprayed in the form of an aqueous flux (note column 3, lines 24-28). Thus, it would have been obvious to one of ordinary skill in the art to select a flux with small particle size, i.e. at

Art Unit: 1754

least 70% of the flux being in the particle size range of 2-4 micrometers, as suggested by Popoola '187 because such particle size would remain in suspension at all times without stirring (note Popoola '187, column 2, lines 18-27). Alternatively, in Seseke-Koyro, it is disclosed that dry application or wet application can be used to apply the fluxing agent on the aluminum components (note Seseke-Koyro, column 3, lines 50-56). Thus, when a dry application is used, it would have been obvious to one of ordinary skill in the art to select a coarse particle size for the fluxing agent of Seseke-Koyro, i.e. average particle size of greater than 15 microns, as suggested by Shimajiri '775 because such particle size is suitable for dry application.

2. Appellants argue that Claims 8-12 are patentable because there is no reasonable expectation that the proposed medication would be successful.

Appellants argue that the primary references disclose potassium fluorozincate fluxes, but the secondary references each relate to a completely different material; thus, one could not have had a reasonable expectation of successfully *forming* alkali metal fluorozincate salts having the claimed particle size distributions even if Popoola or Shimajiri were combined with Seseke-Koyro or Lauzon.

Firstly, Popoola or Shimajiri is applied to teach a desired particle size for the fluxing agent, not to teach the method of making the fluxing agent itself. In the primary references, i.e., Seseke-Koyro or Lauzon, potassium fluorozincate fluxing agent is clearly disclosed. Thus, when the teaching of these primary references is taken in view of the secondary references (Popoola or Shimajiri), it would have been obvious to

Art Unit: 1754

subject the potassium fluorozincate fluxing agent in the primary references to any additional process steps, such as classifying, granulating or pulverizing processes, to obtain the desired particle size as suggested in the secondary references. It should also be noted that in Appellants' specification, it is disclosed that alkali metal fluorozincate produced by the prior art (German Published Application 199 13 111) is coarser than the claimed product (note paragraph bridging pages 4-5). This fairly teaches that a coarser product of fluorozincate is known and available in the art and it would have well within the skilled of the artisan to reduce the fluorozincate coarser particle size to a finer particle size as suggested by Popoola. Secondly, the particle size as suggested in the secondary reference is dependent on the method of applying the fluxing agent, not on the type or composition of the fluxing agent. Thus, one skilled in the art would have reasonable expected that the finer particles would work equally well when the fluxing agent as disclosed in the primary references is used in a wet process instead of the fluxing agent of the Popoola or coarser particle size of the fluxing agent of the primary references in a dry process instead of the fluxing agent of Shimajiri, i.e., the fluxing agent would be successfully applied on the aluminum substrate(s) to be brazed. Lastly, Lauzon '850 fairly teaches that potassium fluorozincate as disclosed in Lauzon '850 or in Seseke-Koyro is an analogous fluxing agent to the potassium fluoroaluminate (note column 1, lines 5-11) as disclosed in the secondary references. Thus, it would have been obvious to one skilled in the art to use the same method for applying the fluxing agent in the secondary references for the analogous fluxing agent in the primary references.

3. Appellants argue that there is no basis to incorporate the particle size of the aluminum-based materials in Popoola into the materials of Seseke-Koyro or Lauzon.

First, Appellants argue that there is no reason to believe that the teachings related to the potassium aluminum fluoride salts of Popoola would even be applicable to the potassium fluorozincate salts as disclosed by Seseke-Koyro and Lauzon.

Again, as stated above, the particle size of fluxing agent is selected based on the method of applying the fluxing agent, not on the type of the fluxing agent. Furthermore, Lauzon fairly teaches that the potassium aluminum fluoride and the potassium fluorozincate are analogous fluxing agents in the art.

Second, Appellants argue that the applied references are silent as to which process conditions to select for optimization, much less how any process conditions might affect particle size.

Controlling the particle size of the product by adjusting the process conditions would have been obvious to one skilled in the art, however, even if the particle size of the product could not be controlled during the process of making it through routine experimentation, it would have been obvious to one skilled in the art to subject the product to additional process steps such as agglomerating, pulverizing, classifying, etc. to obtain a product with the desired particle size.

Finally, Appellants argue that Appellants have unexpectedly discovered that alkali metal fluorozincate salts having a desired particle size can be prepared by drying the product of an aqueous reaction without the need for additional processing (i.e., without pulverizing).

Appellants' alleged unexpected result as stated above is for the process of making the product (i.e., the process does not require a pulverizing step), however, Appellants' claims are to a product, not a process for making it. There is showing or evidence to show that the claimed product is patentably different from the product of the prior art, when the process of the prior art includes a pulverizing step.

A. Appellants argue that claim 8 and 9 are independently patentable because the cited references fail to teach or suggest an alkali metal fluorozincate in which the particles have a diameter of less than 5 micrometers.

Appellants argue that none of the cited references disclose or suggest potassium fluorozincate particles having a diameter of less than 5 micrometers.

As stated in the above rejection, Popoola '187 is applied to teach that the desired particle size for a fluxing agent is preferably controlled to less than 10 micrometers, with at least 70% of such salts being in the particle size range of 2-4 micrometers (note column 2, lines 22-24 and column 3, lines 45-47). These ranges at least overlap the claimed range of "less than 5 micrometers". It would have been obvious to one skilled in the art to combine the teaching of the particle size in Popoola '187 with the teaching of potassium fluorozincate fluxing agent in Seseke-Koyro or Lauzon for the reasons stated above.

Art Unit: 1754

B. Appellants argue that claim 10 is independently patentable because the cited references fail to teach or suggest an alkali metal fluoride metal fluorozincate wherein 50% of the particles have a diameter of less than 3.8 micrometers.

Appellants argue that none of the cited references disclose alkali metal fluorozincate particles having such fine particle size.

Again, Popoola '187 teaches that *at least* 70% of the fluxing salts are in the particle size range of 2-4 micrometers. This fairly suggests the claimed range of "50% of all particles have a diameter < 3.8 μm ". In any event, it would have been obvious to one skilled in the art to optimize the particle size of the fluxing agent within the range of "less than 10 microns" as disclosed in the Popoola '187 in order to maintain the particles in suspension at all times without stirring (note column 2, lines 18-27). It would have been obvious to one skilled in the art to combine the teaching of the particle size in Popoola '187 with the teaching of potassium fluorozincate fluxing agent in Seseke-Koyro or Lauzon for the reasons stated above.

C. Appellants argue that claim 11 is independently patentable because the cited references fail to teach or suggest an alkali metal fluorozincate in which 50% of the particles have a diameter of less than 11 micrometers.

Appellants argue that none of the cited references disclose or suggest alkali metal fluorozincate particles having a grain spectrum in which 50% of the particles have a diameter of less than 11 micrometers.

The disclosure of "less than 10 microns" in Popoola '187 would meet the claimed range of "less than 11 micrometers" in Appellants' claim 11. Again, it would have been obvious to one skilled in the art to combine the teaching of the particle size in Popoola '187 with the teaching of potassium fluorozincate fluxing agent in Seseke-Koyro or Lauzon for the reasons stated above.

D. Appellants argue that claim 12 is independently patentable because the cited references fail to teach or suggest an alkali metal fluorozincate wherein 50% of the particles have a diameter of greater than 11 micrometers.

Appellants argue that none of references teach or suggest an alkali metal fluorozincate having such a grain spectrum, as required in Appellants' claim 12.

Shimajiri '775 is applied as stated above to teach that when a dry process is used to apply a fluxing agent onto an aluminum substrate, the fluxing agent is desired to have a grain size of 15 microns on average (note column 4, lines 55-57). This fairly suggests the claimed range of "50% of all particles have a diameter $> 11 \mu\text{m}$ ". It would have been obvious to one skilled in the art to combine the teaching of the particle size in Popoola '187 with the teaching of potassium fluorozincate fluxing agent in Seseke-Koyro or Lauzon for the reasons stated above.

(11) Related Proceeding(s) Appendix

No decision rendered by a court or the Board is identified by the examiner in the Related Appeals and Interferences section of this examiner's answer.

Art Unit: 1754

For the above reasons, it is believed that the rejections should be sustained.

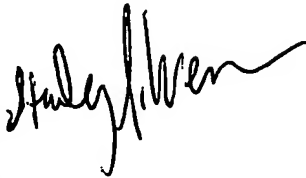
Respectfully submitted,

N. M. Nguyen



Conferees:

Stanley Silverman



Patrick Ryan



PT0 06-4874

CY=WO DATE=19990930 KIND=A1
PN=99-48641

NEW FLUXING AGENTS
[Neue Flussmittel]

Ulrich Seseke-Koyro, et al.

UNITED STATE PATENT AND TRADEMARK OFFICE
Washington, D.C. June 2006

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(19):	WO
DOCUMENT NUMBER	(11):	99/48641
DOCUMENT KIND	(12):	A1
PUBLICATION DATE	(43):	19990930
APPLICATION NUMBER	(21):	PCT/EP99/00851
DATE OF FILING	(22):	19990323
ADDITION TO	(61):	
INTERNATIONAL CLASSIFICATION	(51):	B23K35/363 // 103/10
PRIORITY	(30):	March 256, 19987 [GE] 198 13 023.6
INVENTORS	(72):	SESEKE-KOYRO, ULRICH; FREHSE, JOACHIM; BECKER, ANDREAS
APPLICANT	(71):	SOLVAY FLUOR UND DERIVATE GMBH
DESIGNATED CONTRACTING STATES	(81):	CA, CN, IN, JP, KR, MX, RU, US, ZA, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE
TITLE	(54):	NEW FLUXING AGENTS
FOREIGN TITLE	[54A]:	NEUE FLUSSMITTEL

Specification

The invention relates to new fluxing agents for brazing of aluminum and aluminum alloys, a brazing process and brazed components.

Assemblies (for example, radiators for automotive engines or heat exchangers) of aluminum or aluminum alloy parts can be produced by brazing. Advantageously a fluxing agent based on fluoroaluminate is used which removes oxide adhesions from the surface of the components to be brazed to one another. Potassium fluoroaluminate fluxing agents are especially well suited for aluminum or low-magnesium aluminum alloys. Such a process is disclosed in British patent 1 438 955. Production of the corresponding fluxing agents is described for example by Willenberg US-A 4,428,920 and Meshri, US-A 5,318,764 and by Kawase, US-A 4,579,605.

Fluxing agents which contain cesium fluoroaluminates are described for example in Suzuki, US-A 4,670,067 and Shimizu, US-A 5,171,377. These fluxing agents which can additionally contain potassium fluoroaluminate fluxes are especially well suited to brazing of aluminum alloys with a higher magnesium content.

In brazing, the procedure is applying the fluxing agent (for example, in the form of a suspension) and a brazing metal to the components to be joined. The components are assembled in the desired position and heated. First the fluxing agent melts and cleans the surface, then the brazing solder melts. The parts are cooled. /2

US-A 5,190,596 teaches that instead of a brazing metal a metal can be added to the fluxing agent to form a eutectic when brazing with

* Number in the margin indicates pagination in the foreign text.

aluminum. Suitable metals are copper, zinc, and germanium, especially silicon.

The addition of certain metal fluorosilicates in certain amounts can make the brazing metal superfluous (see EP-A 810 057 and German patent application 196 36 897.9). The latter application discloses that a mixture of potassium fluoroaluminate fluxing agent and potassium fluorosilicate in which the potassium fluorosilicate is contained in an amount from 6 to 50% by weight makes the brazing metal unnecessary.

The initially mentioned British patent 1,438,955 explains that smaller amounts of alkali metal zinc fluorides, up to 5% by mole, in the flux can be tolerated. Their presence however does not yield any advantages with respect to reducing the melting point, rather all would have the effect of raising the melting point. Haramaki, US-A 4,645,119 discloses fluxes based on potassium fluoroaluminate which contain 3 to 30% by weight ZnF_2 , optionally in the form of $KZnF_3$. The zinc fluoride decomposes at the brazing temperature and the metallic zinc covers the brazed parts or the entire surface of the components to be brazed to one another and imparts improved corrosion protection to the aluminum.

The object of this invention is to make available a new application process and new fluxing agents which can be used for this purpose. This object is achieved by the process as claimed in the invention, the new flux and the new fluxing agent.

The process as claimed in the invention for brazing of aluminum and aluminum alloys using a fluxing agent based on complex fluorides calls for the fluxing agent to contain alkali fluorozincate or /3 mixture of alkali fluoride and zinc fluoride as a flux, and brazing is done at a temperature in the range from 420 to 600°C, preferably below

590°C.

That the alkali fluorozincate or mixtures of alkali fluoride and zinc fluoride at these temperatures have fluxing agent action is an unexpected finding. Surprisingly, alkali fluorozincates however act a fluxing agents even if brazing is done at temperatures which are far below the melting point of the alkali fluorozincate used. The melting points of KZnF_3 and K_2ZnF_4 are for example 870°C and 737°C, therefore a brazing process should not take place at temperatures below 600° C. This is for the following reason: in the presence of solder-forming components such as silicon, an Al-Si eutectic forms. Based on electrochemical processes this generates an alkali fluoroaluminate fluxing agent in situ; for example it is assumed that $\text{KZnF}_3 + \text{Al}$ (from the Al-Si alloy) reacts with the formation of KAlF_4 or KF and AlF_3 and Zn metal. But this is only an attempt at an explanation which could explain the phenomenon as a brazing process and the formation of Zn.

Mixtures of the alkali fluoride (or alkali fluorides) and zinc fluoride yield usable brazing. The molar ratio of alkali fluoride to zinc fluoride can be in the range of roughly 1:1, for example from 1:1.05 to 1.05:1. But also one of the two components can be present in a greater excess, especially the zinc fluoride. Preferably however alkali fluorozincates are used since they yield \geq better brazing.

The term "alkali fluorozincate" within the framework of this invention comprises compounds of general formula $(\text{MF})_x \cdot (\text{ZnF}_2)_y$, in which $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and $0 \leq x \leq 4$ and $0 \leq y \leq 4$. "Alkali fluoride" comprises the fluorides of lithium, sodium, potassium, rubidium and cesium.

Preferably x and y are whole numbers, specifically independently $\frac{1}{4}$ of one another 1, 2, 3, or 4; x and y however can also be in a substoichiometric ratio to one another. Either x , y or both are then greater than 0, but do not represent whole numbers. In this case it is preferred if y is greater than x .

The concept of "fluxing agent" within the framework of this invention comprises those compounds which have the surface cleaning action desired in brazing (especially removal of oxide layers). The fluxing agent can consist of alkali fluorozincate; other fluxing agents are then not contained. The fluxing agent can also have other fluxing agents beside alkali fluorozincate. For example, the fluxing agent can constitute a mixture of alkali fluorozincate and alkali fluoroaluminate, for example potassium fluoroaluminate and/or cesium fluoroaluminate. The alkali fluorozincate can be present as a pure compound or as a mixture of alkali fluorozincates. For example, pure potassium fluorozincate or pure cesium fluorozincate can be used. In this connection they can be compounds which are present in one or more phases. For example, pure KZnF_3 or mixtures of KZnF_3 and K_2ZnF_4 can be used. But also the corresponding mixtures with various alkali metal cations can be used.

Preferred fluorozincates are potassium fluorozincate and cesium fluorozincate. They can of course also be contained as a mixture.

If cesium fluorozincate is contained as the sole fluorozincate in the fluxing agent, it is present in an amount of 5 or more 5% by weight. Preferably the alkali fluorozincate is contained in an amount of more than 30% by weight, especially in an amount of 50 or more % by weight in the fluxing agent. The percentages relate to the fluxing

agent set as 100% by weight. If not pure alkali fluorozincate fluxing agents, other fluxing agents constitute the remainder to 100% by weight of the mixture, especially fluxing agents based on potassium and/or /5 cesium fluoroaluminate.

The fluxing agent can often be used as such, without adding consumables. For example, brazing solder-clad aluminum sheets can be brazed with pure fluxing agent. In addition to the fluxing agent, ready-to-use compositions can if desired comprise consumables. The fluxing agent can also contain consumables such as binders, dispersants, brazing metal, brazing metal precursors, solder-forming materials such as metal fluorosilicates, especially alkali fluorosilicates, or stabilizers. In the process as claimed in the invention, fluxing agents of pure alkali metal fluorozincate and fluxing agents which contain in addition potassium fluoroaluminate and/or consumables can be easily used.

If the fluxing agent contains a binder, it is advantageously contained in an amount from 10 to 90% by weight. If the brazing metal is contained in the flux, it is advantageously contained in an amount from 25 to 75% by weight. The fluxing agent, as described in US patents 5,100,048 and 5,190,596, can contain solder-forming metals such as silicon, copper or germanium added. They are then contained in an amount from roughly 10 to roughly 80% by weight. The above described quantitative figures can also be exceeded or not reached. The effective minimum or maximum amount can be determined by manual tests (brazing tests).

A metal fluorosilicate such as alkali fluorosilicate, for example potassium hexafluorosilicate, can also be contained as the brazing

metal precursor. If it is contained, the amount is advantageously in the range from 5 to 95% by weight.

The aforementioned percentages relate to the entire fluxing agent set as 100% by weight.

As is shown in DE application 196 36 897.9, brazing can be done without brazing solder, if at least 6% by weight K_2SiF_6 are contained in the fluxing agent. The same applies according to EP-A 810 057 to /6 fluxing agents which contain 7 to 15% by weight metal fluorosilicates such as Cs_2SiF_6 , $CsHSiF_6$,? or $CsKSiF_6$. For K_2SiF_6 , 25 to 50, even up to 75% by weight are advantageous. But even if metal fluorosilicates are contained in the fluxing agent in small amounts, for example in an amount from 1 to less than 6% by weight, the fluxing agent properties with respect to wetting properties of the surface to be brazed, but also the melting point of the fluxing agent, are benefitted.

In the scheduled use of the fluxing agent in the form of a suspension, also dispersants which stabilize the suspension can be used.

The fluxing agent can be applied to the aluminum or aluminum alloy components to be joined in the conventional manner. Dry application based on electrostatic spraying technology is possible based on the good fluidization properties of the fluxing agents. Alternatively, the fluxing agent can be applied in the form of an aqueous or organic suspension or as a paste to the materials to be joined. Aqueous or organic suspensions advantageously contain 15 to 75% by weight of the fluxing agent. Suspensions of the fluxing agent in organic liquids can also be used, advantageously the substances commonly used as organic solvents, such as alcohols, especially methanol, ethanol, propanol or

isopropanol and polyols. Other organic liquids ("carriers") are ether, for example diethylene glycol monobutyl ether, ketones, such as acetone, esters of alcohols, diols, or polyols. A binder for use as paste is for example ethyl cellulose,. By means of film forming agents, usually polymers which are soluble in organic solvents, for example acetone, fluxing agents with optionally a brazing solder or brazing solder precursor can be applied to the workpiece, and after evaporation of the solvent yield a securely adhering film. Suitable polymers are for example (meth)acrylates. During brazing the film forming agent then evaporates.

In use, the brazing metal, if needed, can be contained in the /7 fluxing agent (as an added powder); it can also be applied as cladding to the components to be brazed or in addition to the fluxing agent.

The brazing temperature depends on the brazing solder used or the solder-forming metal or substance. Below the brazing metal liquidus temperature of 450°C, it is called soldering, above, brazing. There are low melting solders, such as for example zinc aluminate solders which can be used starting at 390°C or pure zinc solder which can be used starting at 420°C for brazing. Other solders can be brazed at a higher temperature. Al-Si-[Cu] solders can be used starting at [530°C] or 575°C.

Generally a brazing temperature up to 600°C is sufficient. Preferable brazing is done at 390°C to 600°C, especially at 420°C to 590°C. Here ambient pressure prevails. Brazing, for example in a vacuum, with vaporization of the fluxing agent as described in JP-A 03/099 795 does not fall within this invention. Flame or furnace brazing can be done especially in an inert atmosphere (for example, N₂

atmosphere).

Known fluxing agents can be used for the process as claimed in the invention. Japanese application 71/293 699 for example discloses fluxing agents consisting of potassium fluoroaluminate in a certain molar ratio. US-A 4,645,119 discloses a fluxing agent based on potassium fluoroaluminate which also contains potassium fluoroaluminate. The potassium fluoroaluminate was used as an additive for corrosion improvement, not as a fluxing agent. European patent application EP-A-0 659 519 discloses a fluxing agent for brazing aluminum which contains potassium fluoride, zinc fluoride and aluminum fluoride within certain ranges. Possibly potassium fluoroaluminates are contained here.

New fluxing agents which can be used in the processes as claimed /8 in the invention and which are likewise the subject matter of the invention are described below.

One subject matter of the invention is a fluxing agent which can be used for brazing of aluminum and aluminum alloys, which contains an alkali metal fluoroaluminate and brazing metal and especially a brazing metal precursor and optionally alkali metal fluoroaluminate and optionally consumables, or which consists thereof. Alkali means preferably potassium, cesium and rubidium. Preferred alkali metal fluoroaluminates are potassium fluoroaluminate and/or cesium fluoroaluminate; the preferred brazing metal precursor is silicon, copper, zinc or germanium or a metal fluorosilicate, preferably an alkali metal fluorosilicate, especially potassium fluorosilicate and/or cesium fluorosilicate. If desired, conventional consumables such as binders, carriers or stabilizers can be contained. Starting with 2% by weight alkali fluoroaluminate, positive effects on the brazing behavior can be

established. The consumables, for example binders, can be contained in an amount from 10 to 90% by weight, relative to the total weight of the fluxing agent. The fluxing agent according to one embodiment contains preferably 5 to 95% by weight alkali fluoroaluminate (as the sole component with fluxing agent activity) and 5 to 95% by weight solder or brazing metal precursor, or it consists of them.

If in addition to the alkali fluoroaluminate and brazing metal or brazing metal precursor, alkali fluoroaluminate is still contained in the fluxing agent, the amounts are preferably 5 to 90% by weight alkali fluoroaluminate, 5 to 90% by weight solder or solder metal precursor, and 5 to 90% by weight alkali fluoroaluminate. The fluxing agent can consist of these components, or consumables can be contained in an amount from 10 to 90% by weight, relative to the total weight of the fluxing agent. According to one especially preferred embodiment, the fluxing agent contains alkali fluoroaluminate, alkali fluoroaluminate and at least one brazing metal precursor. The preferred alkali fluoroaluminate is potassium fluoroaluminate and cesium fluoroaluminate, /9 the preferred brazing metal is silicon, germanium, zinc or copper or an alkali metal fluorosilicate, preferably potassium fluorosilicate or cesium fluorosilicate. The fluxing agent can consist of the aforementioned components. The alkali metal fluoroaluminate is contained preferably in an amount from 2 to 20% by weight, the alkali metal fluoroaluminate in an amount from 20 to 80% by weight and the brazing metal precursor in an amount from 10 to 50% by weight in the fluxing agent. If desired, conventional consumables such as binders, carriers or stabilizers (for the suspension) can be contained, preferably in an amount from 30 to 70% by weight, relative to the entire weight of the

fluxing agent.

Another subject manner of the invention is a fluxing agent which can be used for brazing of aluminum and aluminum alloys and contains more than 5% by weight, preferably more than 5% by mole, but less than 100% by weight cesium fluorozincate and potassium fluoroaluminate or cesium fluoroaluminate as the remainder to 100%. This fluxing agent preferably contains more than 30% by weight, especially 50% or more by weight cesium fluorozincate. The advantage of this fluxing agent which can contain, if desired, conventional consumables such as binders, carriers or stabilizers is that even magnesium-containing aluminum alloys can be very easily brazed. This is attributed to the cesium cation. Therefore alternatively mixtures of potassium fluorozincate and cesium fluoroaluminate can be very easily used.

Assemblies of brazed parts of aluminum or aluminum alloys produced using the fluxing agent as claimed in the invention or the fluxing agent as claimed in the invention [sic] are likewise the subject matter of the invention.

The required alkali fluorozincates can be produced in different ways. For example alkali fluoride, for example cesium fluoride or potassium fluoride, can be melted with zinc fluoride in the desired ratio. Alternatively an aqueous solution can be used. Thus, from an aqueous solution alkali fluorides and zinc fluoride can be /10 reacted with the formation of alkali zinc fluoride and the precipitated alkali zinc fluoride can be isolated if necessary. For this purpose a zinc fluoride solution which as desired has been produced fresh from potassium zinc oxide and aqueous HF will be reacted with a potassium fluoride solution which has been obtained fresh as desired from

potassium hydroxide and aqueous HF. Processing takes place such that the precipitated solid is separated from the supernatant solution and then dried. Another procedure calls for reacting a solution of alkali bifluorides (for example, adducts of HF and alkali fluoride) with zinc oxide. Thus, the alkali fluoride and/or the zinc fluoride can be produced by salting of other alkali or zinc salts by means of HF or alkali or ammonium bifluoride in the solution.

Information about phase diagrams, based on thermal and x-ray analyses, is given by O. Schmidt-Dumont and Horst Bornefeld in Z. anorg. Chem. 287 (1956), pp. 120 to 137. Information about $\text{Cs}_4\text{Zn}_3\text{F}_{10}$ is given by D. Babel in Z. Naturforsch. 20a (1965), pp. 165 and 166. A new method for producing fluorometallates is described by M.K. Chauduri, S.K. Ghosh and Z. Hiese in J. Chem. Soc. Dalton Trans. (1984), pp. 1763 to 1964.

Assumed differently than in the prior art, alkali fluorozincates are suited as fluxing agents for aluminum brazing or brazing of aluminum alloys such as Mg-Al alloys at temperatures of 600°C and less. Working in a vacuum with fluxing agent vapor is not necessary. The residue is not corrosive and can be enamelled over. The range of known fluxing agents will be expanded in the foreseeable future.

The following examples will further explain the invention without limiting its scope.

Examples

/11

Example 1:

Production of potassium fluorozincate (JF 009400)

Zinc oxide is reacted with aqueous HF to form a zinc fluoride solution (solution 1). Solution 1 is added with stirring to an aqueous

KF-HF solution produced beforehand (solution 2 of 23.3 g KF and 16 g HF). It is stirred for another hour and filtered off from the precipitated solid. The solid is dried at 110°C in a air circulation cabinet.

Yield: 95.4% (of theoretical)

Analysis: XRD confirms pure KZnF_3 ; identification with the reference spectrum (see Figure 1/7).

DTA to 650°C no detectable phase conversion.

Example 2:

Production of cesium fluorozincate (JF 009403)

30 g of CsOH are reacted with aqueous HF into $\text{CsF}\cdot\text{HF}$ in solution. While stirring, 16.3 g zinc oxide are added in batches to this solution. Processing takes place as in Example 1.

Yield: 52.8% (of theoretical)

Analysis: 33.9% Cs, 37.9% Zn

XRD according to appendix, no reference spectrum present (see Figure 2/7).

DTA: several onsets, especially at 368.5°C, 558.8°C and 664.6°C.

Example 3:

Production of cesium fluorozincate (JF 009404)

60 g of CsOH are reacted with aqueous HF into $\text{CsF}\cdot\text{HF}$ in solution. While stirring, 16 g zinc oxide are added in batches to this solution. Processing takes place as in Example 1.

Yield: 52.8% (of theoretical)

Analysis: 49.0% Cs, 27.2% Zn

XRD according to appendix, no reference spectrum present (see Figure 3/7).

/12

DTA: small onset 499°C, main peak at 583.8°C.

Example 4:

Production of cesium fluorozincate (JF 009415)

As in Example 3, but stirring continues for 2.5 hours at roughly 90°C. Processing takes place as in Example 1.

Yield: 67.3% (of theoretical)

Analysis: 58% Cs, 26.1% Zn

XRD (see Figure 4/7) no reference spectrum present.

Example 5:

Production of cesium fluorozincate (JF 009418)

45 g of CsOH are reacted with aqueous HF into CsF·HF in solution.

While stirring, 16.3 g zinc oxide are added in batches to this solution and stirring continues for 2 hours at roughly 80°C. Processing takes place as in Example 1.

Yield: 73.5% (of theoretical)

Analysis: 85.5% Cs, 36.2% Zn

XRD, no reference spectrum present (see Figure 5/7).

DTA: Onsets at 502.4°C, 556.3°C and 586.4°C.

Example 6:

Production of sodium fluorozincate (JF 009419)

16 g of NaOH are reacted with aqueous HF into NaF·HF in solution.

While stirring, 32.6 g zinc oxide are added in batches to this solution. Processing takes place as in Example 1.

Yield: 95.0% (of theoretical)

Analysis: XRD, identification with reference spectrum 20 11 82 /13
(see Figure 6/7).

DTA: Onset at 648.4°C

Example 7:

Production of rubidium fluorozincate (JF 009420)

20.5 g of RbOH are reacted with aqueous HF into RbF·HF in solution. While stirring, 16.3 g zinc oxide are added in batches to this solution. Processing takes place as in Example 1.

Yield: 93.8% (of theoretical)

Analysis: XRD, reference spectrum 20 10 16 (see Figure 7/7).

DTA: Peaks at 638.6°C and 683.0°C

Brazing tests**General brazing conditions:**

On an aluminum or AlMg coupon [25x25 mm] with or without solder or solder cladding, a defined amount of the fluxing agent with one to two drops of isopropanol is rubbed onto the coupon surface to obtain a uniform distribution of the fluxing agent on the surface. Then this coupon is provided with an aluminum angle [roughly 45°, length 40 mm, height 5 mm] and the isopropanol is allowed to evaporate. This coupon is then placed in a preheated brazing furnace [roughly 400°C for ZnAl brazing, roughly 520°C for AlSi(Cu) brazing] through which a controlled atmosphere [nitrogen dewpoint -40°C] is passed [so-called CAB brazing] and is heated to the brazing temperature [brazing of the angle with the coupon, depending on the solder up to 600°C [so-called CAB brazing process]]. Nocolok^r is potassium fluoroaluminate.

Flux/coverage	3g/m ² Al3003+Al angle	5 g/m ² Al3003+Al angle	7 g/m ² Al3003+Al angle	5 g/m ² Al3003+solder+Al angle
JF 009400 KZnF ₃			Lot AlSi12 zu 100 % verbleist	sehr gut gelötet
JF 009403 CeZnF ₃			inhomogene Lötverf.	behtestigand gelötet, 6 m/h
JF 009404 Cs ₂ ZnF ₄		ZnAl 5/2 zu 100 % verbleist		sehr gut gelötet
JF 009415 CaZnF ₃			1,5 cm nicht verbleist	1,5 cm nicht verbleist
JF 009400 JF 009400+ Si-Pulver 2:1	sehr gut gelötet, 100%	sehr gut gelötet, 100 % zuviel Lot		sehr gut gelötet, 100 % zuviel Lot
JF 009400 JF 009400+ AlSi12 1:1		sehr gut gelötet, 100 %		sehr gut gelötet, 100 %
JF 009403 JF 009403+ AlSi12 1:1		nicht gelötet		1,5 cm nicht gelötet
JF 009404 JF 009404+ AlSi12 1:1		1,5 cm nicht verbleist	>90 % gelötet	sehr gut gelötet, 100 %
KF+ZnF ₂ (Verreibung)		nicht gelötet		sehr gut gelötet, 100 %
JF 009404+ JF 009404+ K ₂ SiF ₆ 1:2 Verreibung		Bei 15 g/m ² sehr gut gelötet		
CsAlF ₄ / JF 009404			ZnAl 6-Lot zu 100 %, Zn-Lot zu 100 %	Zn-Lot nicht gelötet

Key for first five columns + 10 lines:

Flux/coverage	3g/m ² Al3003+Al angle	5 g/m ² Al3003+Al angle	7 g/m ² Al3003+Al angle	5 g/m ² Al3003+solder+Al angle
JF 009400 KZnF ₃				SolderAlSi12 based to 100%
JF 009403 CeZnF ₃				
JF 009404 Cs ₂ ZnF ₄		ZnAl 5/2 brazed to 100%		
JF 009415 CaZnF ₃				
JF 009400 JF 009400+ Si powder 2:1	very well brazed, 100%	very well brazed, 100% too much solder		
JF 009400 JF 009400+ AlSi 12 1:1			very well brazed, 100%	
JF 009403 JF 009403+ AlSi12 1:1			not brazed	
JF 009404 JF 009404+ AlSi12 1:1		1.5 cm not brazed	>90% brazed	
KF+ZnF ₂ (Rubbing)			not brazed	
JF 009404+ JF 009404+ K ₂ SiF ₆ 1:2 rubbing			At 15 g/m ² very well brazed	
CsAlF ₄ / JF 009404				ZnAl 6 solder to 100%, Zn solder to 100%

Key for second 5 columns + first ten lines:

6 g/m ² Al clad w/ 4050+Al angle	10 g/m ² Al clad w/ 4050+Al angle	10 g/m ² AlMg1+solder+AlMg 1 angle	10 g/m ² AlM1+solder+AlMg 1 angle	6 g/m ² Al+solder AlMg1 angle
very well brazed		Zn solder, 1.5 cm not brazed		
nonuniform solder seam	satisfactorily brazed, 6 min			
very well brazed				
1.5 cm not brazed	1.5 cm not brazed			
very well brazed, 100% too much solder		not brazed		
very well brazed, 100%				
1.5 cm not soldered				
very well brazed, 100%				
very well brazed, 100%				

Prozessname	1. Schritt	2. Schritt	3. Schritt	4. Schritt	5. Schritt	6. Schritt	7. Schritt	8. Schritt	9. Schritt
JF 009404 JF 009404/Nocolok ^R 1:1 Mischung				Lot 4145 100 % gelötet			nicht gelötet	AlSi12 zu 80 % verlotet	Lot AlSi12 zu 100 % verlotet
JF 009400 JF 009400/K ₂ SiF ₆ 1:2 V22-Rubbing		sehr gut gelötet 100 %							
JF 009400 JF 009400/Nocolok ^R 1:1 Mischung				Lot 4145 zu 100 % gelötet					
JF 009418				zu 100 % verlotet	zu 100 % verlotet				
JF 009419						nur punktuelle Verlotung			
JF 009420				Lot AlSi12 zu 100 % verlotet	zu 100 % verlotet		15 g/m ² m. Lot AlSi12, Coupon + Winkel 6063 zu 100 % verlotet	m3 Lot AlSi12, Coupon 6063 + Al-Winkel 100 % verlotet	
JF 009404 JF 009404+ Si-Pulver 2:1			gut gelötet, 60 %						
JF 009400 JF 009400+ Si-Pulver 2:1			gut gelötet, 100 %						
JF 009404 JF 009404+ Si-Pulver 2:1			gut gelötet, 60 %						

Key for all 9 lines of page 15, first 5 columns (Header is same as page 14 table)

JF 009404 JF 009404/ Nocolok ^R 1:1 mixture				Solder 4145 100% brazed
JF 009400 JF 009400/ K ₂ SiF ₆ 1:2 rubbing				
JF 009400 JF 009400/ Nocolok ^R 1:1 mixture				solder 4145 bazed to 100%
JF 0094018				brazed to 100%
JF 009419				
JF 009420				Solder AlSi12 brazed to 100%
JF 009404 JF 009404+ Si powder 2:1			well brazed, 60%	
JF 009400 JF 009400+ Sil flux 2:1			well brazed, 100%	
JF 009404 JF 009404+ Sil flux2:1			well brazed, 60%	

Key for last 5 columns:

		not brazed	AlSi 12 brazed to 50%	Solder AlSi 100% brazed
brazed to 100%				
	only spot brazing			
brazed to 100%		15 g/m ² w/solder AlSi12, Coupon + angle 6063 brazed to 100%	w/ solder AlSi12 Coupon 6063+Al angle 100% brazed	

1. Process for brazing of aluminum and aluminum alloys, the fluxing agent containing alkali fluorozincate or mixtures of alkali fluoride and zinc fluoride, and brazing being done at a temperature in the range from 390°C to 600°C, preferably from 420 to 600°C.

2. Process as claimed in Claim 1, wherein potassium and/or cesium fluorozincate is contained in the fluxing agent.

3. Process as claimed in Claim 1, wherein if cesium fluorozincate is contained in the fluxing agent, it is present in an amount of more than 5% by mole.

4. Process as claimed in Claim 1, wherein the potassium fluorozincate and/or cesium fluorozincate is contained in an amount of more than 30% by weight in the fluxing agent.

5. Process as claimed in Claim 4, wherein the potassium fluorozincate and/or cesium fluorozincate is contained in an amount of 50% or more by weight in the fluxing agent.

6. Process as claimed in Claim 1, wherein the fluxing agent consists of an alkali fluorozincate or of alkali fluorozincate and consumables.

7. Process as claimed in Claim 1, wherein brazing is done at a temperature in the range from 420 to 590°C.

8. Process as claimed in Claim 1, wherein in addition to the alkali fluorozincate, potassium fluoroaluminate or cesium fluoroaluminate is contained in an amount up to 95% by weight.

9. Process as claimed in Claim 1 or 6, wherein the fluxing agent contains consumables such as binder, brazing metal, brazing metal precursors or stabilizers for suspensions. /17

10. Process as claimed in Claim 9, wherein the fluxing agent contains metal fluorosilicate, preferably alkali fluorosilicate.

11. Modification of the process as claimed in Claim 1 for solder-free brazing of aluminum and aluminum alloys, the fluxing agent containing metal fluorosilicate, preferably alkali fluorosilicate, especially potassium fluorosilicate, in an amount of at least 5 to 95% by weight as the brazing metal precursor.

12. Process as claimed in Claim 1, wherein the fluxing agent is used in the form of an aqueous or alcohol suspension.

13. Process as claimed in Claim 1, wherein brazing is done in a controlled atmosphere or in a non-oxidizing flame.

14. Process as claimed in Claim 1, wherein Mg-containing alloys of aluminum are brazed.

15. Fluxing agent usable for brazing of aluminum and aluminum alloys, containing or consisting of alkali metal fluoroaluminate, brazing metal precursor and optionally alkali metal fluoroaluminate.

16. Fluxing agent usable for brazing of aluminum and aluminum alloys, containing more than 5% by mole, preferably more than 30% by weight, but less than 100% by weight cesium fluoroaluminate.

17. Fluxing agent containing or consisting of 5 to 95% by weight alkali fluoroaluminate and 5 to 95% by weight brazing metal, brazing metal precursor, such as silicon, copper, zinc, and/or germanium, or alkali fluorosilicate.

18. Fluxing agent as claimed in Claim 15, wherein it contains 5 to 90% by weight alkali fluoroaluminate, 5 to 90% by weight brazing metal precursor, and 5 to 90% by weight potassium fluoroaluminate or consists thereof.

19. Fluxing agent containing 5 to 95% by weight alkali fluorozincate and 95 to 5% by weight alkali fluorosilicate, or consisting thereof.

20. Fluxing agent as claimed in one of Claims 15 to 19, wherein alkali stands for potassium, cesium or rubidium.